Reactions of silane with the W(110) surface *

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Reactions of silane with the W(110) surface have been studied using temperature programmed desorption, Auger electron spectroscopy and low energy electron diffraction. At 350 K, silane undergoes complete dissociation on the clean W(110) surface, with an initial dissociation probability of one. The hydrogen atoms produced by silane dissociation are displaced from the surface by silicon atoms during large silane exposures. As the silicon coverage increases, the silane dissociation probability remains > 0.5 until a monolayer of silicon is deposited. The weak dependence of dissociation probability on silicon coverage suggests that dissociation occurs via a mobile precursor. Once the first monolayer is complete, the silane dissociation probability decreases sharply to less than 0.01. At 120 K, silane undergoes only partial dissociation. The resulting adsorbed species are tentatively identified as silyl (SiH₃) groups. The silyl groups decompose during temperature programmed desorption at 200–300 K to evolve H₂ and leave adsorbed silicon atoms on the surface. Adsorbed silicon atoms form a number of ordered overlayer structures, depending on both the silicon and hydrogen coverages and the temperature to which the overlayers are annealed. Heating silicon overlayers to 1050 K results in reaction between silicon and tungsten to form epitaxial tungsten silicide overlayers. Repeated cycles of silane adsorption followed by annealing to 1050 K result in the epitaxial growth of stoichiometric WSi₂ layers on the surface.

1. Introduction

The interface between metals and semiconductors is extremely important in the formation of electronic devices. Reactions between metals and silicon to form metal silicides, resulting in the formation of Schottky barriers at the interface, can affect the electronic properties of the interface. Metal silicides may also have applications as gate materials in VLSI applications due to their low resistivities relative to doped silicon [1]. The vast majority of studies of the metal semiconductor interface have involved adsorption of metals on semiconductor surfaces. An extensive literature exists regarding these types of studies, and a number of excellent review articles are available [2–6]. In contrast, the deposition of semiconductors on metal surfaces has received relatively little attention [7–18]. In addition to applications in the semiconductor industry, the adsorption of semiconductors on metals has interesting implications for corrosion and carburization inhibition [19,20] and for the development of alternative catalytic materials [21,22]. A study of the reactions of silane with W(110) was therefore undertaken in order to further the understanding of the chemical and physical properties of semiconductor modified metal surfaces.

In this paper it will be shown that silane undergoes complete dissociation on W(110) at 350 K, resulting in the formation of ordered silicon overlayers. At 350 K dissociation occurs via a mobile precursor, resulting in dissociation probabilities ≥ 0.5 for silicon coverages up to one monolayer.

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(one monolayer (ML) = \(1.42 \times 10^{15}\) cm\(^{-2}\) for W(110)). For silicon coverages greater than one monolayer the dissociative sticking probability falls to less than 0.01. At 120 K, only partial dissociation of silane occurs resulting in a surface species which is tentatively identified as an adsorbed silyl group. The silyl group completely dissociates by 400 K, evolving H\(_2\) and leaving adsorbed silicon atoms on the surface. Upon heating to 1050 K, reaction between silicon and tungsten results in formation of epitaxial tungsten silicide layers. Stoichiometric WSi\(_2\) layers can be grown by alternately exposing the surface to silane at 350 K and then annealing to 1050 K. This ability to grow tungsten silicide by reaction of silane with metallic tungsten may have applications for chemical vapor deposition (CVD) of silicide films. In a subsequent paper, the effects of adsorbed silicon atoms on the chemisorptive and catalytic properties of W(110) will be reported [23].

2. Experimental

The experiments were performed in an ion pumped ultra high vacuum (UHV) chamber [24] equipped with facilities for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). The mass spectrometer used for TPD is multiplexed to allow up to fifteen masses to be monitored simultaneously. In addition, a collimating aperture is located in front of the mass spectrometer ionizer. By placing the crystal directly in front of this aperture during TPD experiments, desorption from the back and sides of the crystal and the crystal supports can be excluded from the TPD curves. Silane was dosed onto the crystal through a capillary array doser. By placing the crystal directly in front of the doser, the silane pressure at the crystal was enhanced by a factor of approximately 100 over the background pressure. All silane exposures reported in this work have been corrected for this enhancement and for the ionization probability of silane [25].

The W(110) crystal (Metal Crystals Ltd.) was cut and polished using standard techniques. Both resistive heating and electron bombardment could be used to heat the crystal. The main impurity in the crystal was carbon, which was removed by heating to 1800 K in 1 \(\times 10^{-8}\) Torr of oxygen for one to two minutes, followed by annealing to 2300 K to remove adsorbed oxygen. Following oxidation and annealing the C(272 eV)/W(169 eV) AES ratio was generally less than 0.02, no oxygen was detectable, and the crystal displayed a very sharp (1 \(\times 1\)) LEED pattern. Oxygen (Matheson, Research Purity), hydrogen (Matheson, Ultra, High Purity) and silane (Matheson, Semiconductor Purity) were used as received.

Silane adsorption was investigated at 350 K and 120 K. An adsorption temperature of 350 K was chosen rather than the more customary temperature of 300 K in order to assure complete dissociation of silane. It was found that at 300 K only a portion of the silane dissociated completely, resulting in a surface covered by Si and H atoms as well as partially dissociated SiH\(_x\) fragments. At 120 K only partial dissociation of silane to SiH\(_x\) occurs (section 3.2).

For adsorption at 350 K the experimental procedure involved exposing the surface to silane, and then cooling to 120 K prior to recording an AES spectrum and LEED pattern. A TPD experiment was then performed, monitoring H\(_2\), Si, and SiH\(_4\) desorption. The maximum temperature of 700 K reached during TPD was sufficient to quantitatively remove hydrogen from the surface. After TPD, the crystal was cooled to 120 K, and a second AES spectrum and LEED pattern were recorded. Finally, the crystal was heated briefly to 1050 K, recooled to 120 K, and a final AES spectrum and LEED pattern were recorded.

The experimental procedure for investigating silane adsorption at 120 K was to expose the crystal to silane, and then record an AES spectrum and LEED pattern with the crystal still at 120 K. A TPD experiment was then performed with a maximum temperature of 1050 K. After TPD, the crystal was cooled to 120 K, and another AES spectrum and LEED pattern were recorded. In some cases, the TPD experiment was stopped when the temperature reached 700 K in order to investigate the effects of intermediate annealing temperatures.
The surface was cleaned after each experiment by flashing to 2300 K. This treatment was generally sufficient to desorb silicon and cause small amounts of carbon, which occasionally built up on the surface, to diffuse into the bulk. In cases where flashing to 2300 K did not result in a clean surface, the oxidation treatment described earlier was used to produce a clean surface.

3. Results

3.1. Adsorption at 350 K

Fig. 1a shows the variation of the Si(92 eV)/W(169 eV) Auger peak ratio (hereafter referred to as the Si/W ratio) as a function of silane exposure at 350 K. The Si/W ratio shows a linear increase with exposure, up to a ratio of approximately 5.5 following a 6 langmuir (1 langmuir = 1 L = 10⁻⁶ Torr · s) dose. At this point a sharp break occurs in the Auger ratio plot, and the rate of increase in the Si/W ratio with exposure decreases by more than two orders of magnitude. The silane exposure of 6 L required to reach the break point will be referred to as a saturation exposure.

Fig. 2 shows the thermal desorption of hydrogen following adsorption of silane at 350 K. The silane exposures and resulting silicon coverages are (a) 1.0 L, 0.27 ML; (b) 2.0 L, 0.44 ML; (c) 3.0 L, 0.59 ML; (d) 4.0 L, 0.72 ML; (e) 5.0 L, 0.83 ML; (f) 6.0 L, 1.0 ML. The thermal desorption spectrum from hydrogen saturated clean W(110) is shown by the dashed line.
of the silicon is removed from the surface by 1900 K. After heating to 2300 K no silicon is detectable by AES. These results are in qualitative agreement with the work of Hashimoto et al. [11], who studied the adsorption of silicon on polycrystalline tungsten using TPD, and the field emission microscope studies of Swenson and Sinha [17] and Neumann [9]. Hashimoto et al. [11] observed desorption of silicon multilayers at ~1500 K, and a peak which they attribute to silicide decomposition at ~1800 K. Both field emission studies [9,17] report complete desorption of silicon by 2000 K. Dissolution of a portion of the silicon into the bulk during heating cannot be ruled out, but the absence of any detectable buildup of silicon in the near surface region throughout the course of these experiments indicates that the extent of dissolution is very small.

The decrease in hydrogen desorption with increasing silane exposure can best be explained by assuming that silane undergoes complete dissociation on W(110) at 350 K, and the resulting hydrogen and silicon atoms then compete for adsorption sites on the surface. For low exposures, enough adsorption sites are available to accommodate all of the hydrogen and silicon atoms. As the exposure increases, however, the total number of hydrogen and silicon atoms eventually exceeds the number of available adsorption sites, and hydrogen, being the more weakly bound species, is displaced from the surface.

The silicon coverage at saturation can reasonably be taken to be one monolayer on the basis of several observations. First, the nearly complete displacement of hydrogen from the surface at saturation suggests that all hydrogen adsorption sites are blocked by silicon atoms. Since a monolayer of hydrogen can be adsorbed on W(110) [26], at least a monolayer of silicon would be required to block all of the hydrogen adsorption sites, unless it is assumed that one silicon atom can block more than one hydrogen adsorption site. Sterically, however, a silicon atom is not large enough relative to a tungsten atom to block two sites [27], and the very small electronegativity difference between tungsten and silicon [28] makes a strong electronic effect unlikely. Thus, it appears that one silicon atom is required to displace each hydrogen atom, and the saturation silicon coverage must be one monolayer.

A second reason for taking the saturation silicon coverage to be one monolayer arises from an estimate of the dissociative sticking probability of silane on W(110). Using the initial slope of curve a in fig. 1 and measured Auger sensitivity factors for silicon and tungsten [29], the dissociative sticking probability of silane on clean W(110) can be estimated to be of the order of one [30]. In contrast, the dissociative sticking probability of silane on Si(111)-(7 × 7) is < 10^{-5} [31] at 300 K. Thus, for silicon coverages below one monolayer exposed tungsten atoms must be present and dissociation is expected to be rapid. After completion of the first monolayer, impinging silane molecules see a surface which resembles bulk silicon and dissociation is therefore slow. The assumption of a silicon coverage of one monolayer at saturation can therefore easily explain the sharp break observed in fig. 1a at an exposure of 6 L.

A third reason for assignment of the saturation silicon coverage as one monolayer comes from CO adsorption experiments to be reported elsewhere [23] which show that a saturation silane dose on W(110) completely suppresses CO adsorption, while smaller silane doses result in a surface which can still adsorb CO. Similar behavior was observed on polycrystalline tungsten [32]; CO adsorption was completely suppressed by the presence of a monolayer of silicon, while lower silicon coverages still allowed some CO adsorption. By analogy, the complete suppression of CO chemisorption following a saturation silane exposure on W(110) [23] suggests that the saturation silicon coverage on W(110) is close to one monolayer.

Annealing the surface after adsorption of silane at 350 K results in changes in the Si/W ratio which depend on both the annealing temperature and the silane exposure, as shown in figs. 1a–1c. The absence of silicon desorption from the surface below 1600 K, either as elemental silicon or as silane, provides strong evidence that these changes are due solely to alteration of the silicon adlayer, and not to desorption processes.

For low silane exposures, annealing to 700 K results in an increase in the Si/W ratio, while for exposures near saturation, the Si/W ratio de-
increases upon annealing to 700 K (fig. 1b). The changes in the Si/W ratios upon annealing are accompanied by changes in the Si(92 eV) peak shape. These changes are shown in figs. 3a–3c for a silane exposure of 3.0 L. Upon adsorption at 350 K, the Si(92 eV) peak shape is similar to that observed for bulk silicon [29] except that the portion of the peak above the baseline is larger than expected. Upon annealing to 700 K, the increase in the Si(92 eV) peak to peak height is accompanied by an increase in the ratio of the peak rise above the baseline to the drop below the baseline.

It is tempting to attribute the increases in the Si/W ratio upon annealing to 700 K to diffusion of dissolved silicon out of the tungsten substrate. This explanation is unlikely, however, given that no silicon can be detected by AES following annealing to 2300 K, indicating that the near surface region of the W(110) crystal is free of dissolved silicon. Also, the peak shape change which accompanies annealing suggests that a change in the chemical environment of the silicon is occurring, rather than simply a change in coverage.

Thus, an explanation for the increases in the Si/W ratio upon annealing to 700 K must be found which is consistent with a change in the chemical environment of the silicon, and also with the fact that the increase occurs only for low silane exposures. As shown in fig. 2, annealing to 700 K results in complete removal of hydrogen from the surface. Since it is known that adsorbed hydrogen decreases the Si(92 eV) signal on bulk silicon [33–35], removal of hydrogen from the surface upon annealing is consistent with the increase in the Si/W ratio observed here. Furthermore, it is clear that removal of hydrogen from bulk silicon results in an increase in the ratio of the Si(92 eV) peak rise above the baseline to the drop below the baseline [33,35], again consistent with the behavior observed here. Finally, TPD shows that for silane exposures near saturation, very little hydrogen remains on the surface following adsorption. For this reason, an increase in the Si/W ratio is not observed upon annealing to 700 K for high silane exposures. In fact, a decrease in the Si/W ratio is actually observed, which can be attributed to the beginnings of tungsten silicide formation. Presumably silicide formation is also beginning to occur for lower silane exposures, but cannot be detected due to the simultaneous increase in the Si/W ratio caused by removal of hydrogen from the surface. Silicide formation will be discussed further below.

The earlier assertion that silane undergoes complete dissociation at 350 K appears to be inconsistent with the proposed effect of adsorbed hydrogen on the Si(92 eV) peak size and shape, since the effects of adsorbed hydrogen on the Auger spectrum of bulk silicon are due to a bonding interaction between silicon and hydrogen [35]. If complete dissociation is occurring, this bonding interaction should be absent, and no change in the Si(92 eV) peak should be observed upon removal of hydrogen. In order to resolve this inconsistency, it must be assumed that while silane does indeed dissociate, some interaction still exists between the silicon and hydrogen atoms such that the electronic structure, and therefore the Auger spectrum, of the silicon atoms is modified in the presence of hydrogen. Evidence for interactions between adsorbed silicon and hydrogen atoms is presented in sections 4.1.1 and 4.1.2.

An understanding of the effects of adsorbed hydrogen on the Si/W ratio allows calibration of silicon coverages. Calibration was accomplished by comparing measured Si/W ratios with the Si/W ratio obtained for a monolayer of silicon, and assuming that the Si/W ratio varies linearly with coverage. This assumption is, of course, strictly valid only for low silicon coverages. The W(196 eV) signal decreases by only 30% as the silicon coverage varies from zero to saturation, however, so that errors due to deviations from linearity at high coverages should be of a similar magnitude.

Since the Si/W ratio for a monolayer of silicon was obtained in the absence of hydrogen, the Si/W ratios used for calibration should also be obtained in the absence of hydrogen. Thus, for high silane exposures (> 4 L), where most of the hydrogen is displaced during adsorption, Si/W ratios measured after adsorption at 350 K (fig. 1a) were used to calibrate coverages, while for low silane exposures (< 4 L), where more than 0.25 ML of hydrogen remain on the surface following adsorption, Si/W ratios measured after annealing
to 700 K (fig. 1b) were used for calibration. Coverages calculated in this manner are shown in fig. 1. Variations in the Si(92 eV) peak shape with coverage, deviations of the Si/W ratio versus coverage relationship from linearity at high coverages, the possibility that silicide formation is beginning to occur at 700 K, and the somewhat arbitrary choice of a 4 L exposure as the transition point between using curve a and curve b of fig. 1 to determine coverage clearly introduce some uncertainty into the coverage calibration. Note, however, that even if the linear increase in the Si/W ratio shown in fig. 1a is not merely fortuitous, and does, in fact, indicate a linear variation of coverage with exposure, the error introduced by using the calibration procedure described above will be less than 25 percent for all exposures. Fortunately, errors of this magnitude are not large enough to alter the conclusions of this paper.

Using coverages as calculated above and the fact that 1 L of silane corresponds to \(3.5 \times 10^{14}\) molecules/cm\(^2\), the sticking probability (S) of silane on clean W(110) can be estimated to be close to unity. As the silicon coverage increases, S decreases slightly, but remains ≥ 0.5 at coverages near saturation. This dependence of S on coverage is clearly much weaker than the \((1 - \theta)\) or \((1 - \theta)^2\) dependencies predicted by simple Langmuir adsorption models, indicating that silane dissociation probably occurs via a mobile precursor [36].

For all silicon coverages, annealing to 1050 K results in decreases in the Si/W ratio from those observed after annealing to 700 K (cf. figs. 1b and 1c). These decreases are not due to desorption of silicon, as no silicon containing species are observed by TPD below 1600 K. Instead, the decreases are believed to be due to diffusion of silicon into the tungsten substrate to form tungsten silicide. Reactions between silicon and tungsten to form tungsten silicides occur readily at 1050 K [37,38], and formation of metal silicides is known to occur by diffusion of silicon into the metal [5,6]. In addition, a field ion microscope (FIM) study has shown that WSi\(_2\) is formed upon heating a tungsten tip covered by silicon to 950 K [7]. Formation of the silicide is accompanied by the emergence of a small AES feature at 81 eV (fig. 3c). In some cases, the 81 eV feature begins to appear even after annealing to 700 K. Together with the decrease in the Si/W AES ratio upon annealing high coverages of silicon to 700 K, this change in the Si(92 eV) line shape indicates that silicide formation is beginning to occur even at 700 K.

Diffusion of silicon into the substrate to form tungsten silicide must expose some tungsten atoms at the surface, which might be expected to promote additional silane dissociation. Upon annealing the saturated surface to 1050 K and then cooling to 350 K, further exposure to silane does indeed result in an increase in the Si/W ratio. The Si/W ratio continues to increase until an additional 6 L of silane has been dosed, at which point no further increases in the Si/W ratio are observed.

Sequential annealing of the surface to 1050 K followed by a 6 L silane exposure at 350 K gives similar results regardless of how many times the process is repeated; annealing to 1050 K always
reduces the Si/W ratio due to silicide formation, while subsequent exposure to silane at 350 K increases the Si/W ratio, due to dissociation of silane on exposed tungsten atoms sites. In fact, after three to four cycles of annealing and adsorption, the Si/W ratio observed after annealing to 1050 K becomes constant at approximately 4.9, suggesting the formation of a stoichiometric compound.

It should be noted that additional dissociation of silane does not occur if the surface is annealed to only 700 K. After annealing the saturated surface to 700 K in order to remove adsorbed hydrogen, further exposure to silane at 350 K results in no measurable change in the Si/W ratio. Evidently very few surface tungsten atoms are uncovered by annealing to 700 K, indicating that the extent of silicide formation at 700 K is small.

3.2. Adsorption at 120 K

The adsorption of silane on W(110) at 120 K results in behavior very different from that observed at 350 K. The Si/W ratios as a function of exposure at 120 K are shown in figure 1d. The Si/W ratio increases with exposure up to a ratio of 0.4 for a 2.4 L dose, but does not show any further increase for higher exposures. The fact that the Si/W ratio saturates demonstrates that multilayers of silane are not stable at 120 K.

Annealing to 700 K after adsorption at 120 K results in an increase in the Si/W ratio for all exposures. This increase is accompanied by a noticeable change in the Si(92 eV) peak shape, which is shown in figs. 3d and 3b. Upon adsorption at 120 K, the silicon peak shape is quite symmetric about the baseline, with some apparent structure in the portion of the curve above the baseline (fig. 3d). After annealing to 700 K, the peak shape is very similar to that shown in fig. 3b. Annealing to 1050 K after silane adsorption at 120 K also increases the Si/W ratio as shown in fig. 1e, but this increase is less than that observed for annealing to 700 K. The Si(92 eV) peak shape observed after annealing to 1050 K is similar to that for adsorption at 350 K followed by annealing to 1050 K (cf. figs. 3c and 3e), indicating that silicide formation occurs in both cases.

Thermal desorption of hydrogen following adsorption of silane at 120 K is shown in fig. 4. For a 1.0 L dose, a single hydrogen desorption peak is observed at 400 K. For exposures of 2.4 L or greater (saturation), two additional features appear in the hydrogen TPD at 250 K and 300 K. The total area under the TPD peak following a 2.4 L dose corresponds to a monolayer of hydrogen [26].

The presence of a monolayer of hydrogen following a saturation silane dose at 120 K indicates that at least 0.25 ML of silane has been adsorbed, a result consistent with the coverage suggested by AES. While the Si/W ratio measured immediately following a saturation exposure at 120 K is well below the value observed for 0.25 ML of silicon adsorbed at 350 K, the silicon peak shape is also quite different. Thus, without measurement of AES spectra in the N(E) mode, quantitative comparison of the AES spectra measured following adsorption at 350 K and 120 K is not possible. Qualitatively, however, the difference in peak shape indicates a different chemical environment for silicon following adsorption at 120 K versus

![Fig. 4. Thermal desorption of hydrogen following adsorption of silane at 130 K. Silane exposures are (a) 1 L, (b) 2.4 L.](image-url)
Adsorption at 350 K. One possible conclusion which can be drawn is the while complete dissociation of silane occurs at 350 K, only partial dissociation occurs at 120 K resulting in the formation of stable SiH₅ fragments.

3.3. LEED

Adsorption of silane on W(110) at 350 K results in the formation of a number of ordered LEED patterns. The symmetry of the overlayer

Fig. 5. LEED patterns observed following adsorption of silane at 350 K, and proposed overlayer structures. Representative substrate diffraction features are indicated by arrows. The open circles represent tungsten atoms, while the hatched circles represent silicon atoms. The relative sizes of the tungsten and silicon atoms are based on covalent radii taken from ref. [27]. The LEED patterns, beam energies and silicon coverages are (a) \((\frac{1}{2} - \frac{1}{2})\), 215 eV and 0.44 ML; (b) \((\frac{1}{2} - \frac{1}{2})\), 224 eV and 0.72 ML; (c) p\((2 \times 2)\), 232 eV and 1.0 ML.
unit cell often differs from that of the substrate unit cell, necessitating the use of matrix notation to describe the LEED patterns [39]. With the exception of the \(p(2 \times 2)\) pattern, matrix notation will be used to describe all LEED patterns, even though other notations are possible for certain patterns. For instance, the \(\left( \frac{1}{3} \right)\) and \(\left( \frac{2}{3} \right)\) patterns can also be described as \(c(2 \times 2)\) and \(c(4 \times 4)\) patterns, respectively. The substrate unit cell vectors are taken to point along the directions of the close packed rows on the W(110) surface.

No LEED spots due to the overlayer are observed following adsorption at 350 K for silicon coverages less than 0.20 ML. For silicon coverages of 0.27 ML and 0.44 ML, however, a \(\left( \frac{1}{3} \right)\) pattern (fig. 5a) is formed following adsorption at 350 K. At 0.27 ML, this pattern displays broadening of the overlayer spots due to disorder in the \([\overline{1}0]\) direction. As the coverage is increased from 0.44 ML to 0.72 ML additional spots indicative of a \(\left( \frac{1}{3} \right)\) pattern (fig. 5b) gradually appear. For a monolayer of silicon, the pattern shown in fig. 5c is observed following adsorption at 350 K. The locations of the spots are typical of a \(p(2 \times 2)\) pattern, but some of the spots are broadened in the \([111]\) and \([\overline{1}11]\) directions, and small rings can be seen around the substrate spots. In some cases, the spots appear to be split rather than broadened.

Upon heating to 700 K, the \(\left( \frac{1}{3} \right)\) patterns observed for 0.27 ML and 0.44 ML of silicon...
change to \((\frac{1}{2}, -\frac{1}{2})\) and \((\frac{1}{2}, \frac{3}{2})\) patterns, respectively (figs. 6a and 6b). For 0.59 ML and 0.72 ML coverages, annealing to 700 K converts the \((\frac{1}{2}, -\frac{1}{2})\) pattern to a \((\frac{1}{2}, \frac{3}{2})\) pattern (fig. 6c). A \(p(2 \times 2)\) pattern with disorder in the [110] direction appears upon annealing 1.0 ML of silicon to 700 K (fig. 6d). The changes in the LEED patterns upon annealing to 700 K are most likely due to removal of hydrogen from the surface. Lateral interactions between hydrogen and silicon could force the silicon atoms to occupy different sites in the presence of hydrogen than on a hydrogen free surfaces. Since the extent of silicide formation at 700 K is quite small (section 3.1), silicide formation is an unlikely explanation for the changes in the LEED patterns.

For a 0.44 ML coverage, annealing to 1050 K produces the complex LEED pattern shown in fig. 7a. At lower coverages, this pattern is also evident, but not fully developed. For coverages between 0.59 ML and 0.83 ML, annealing to 1050 K produces a \((\frac{1}{2}, -\frac{3}{2})\) pattern (fig. 7b), while annealing a monolayer of silicon to 1050 K forms a \((-\frac{1}{6}, -\frac{1}{6})\) pattern (fig. 7c). Since it was shown above that silicide formation occurs upon heating to 1050 K, these patterns can be attributed to the formation
of tungsten silicide layers on the W(110) substrate. After a saturation silane dose followed by annealing to 1050 K, further exposure to silane at 350 K results only in a large increase in the background signal of the \((-\frac{5}{6}, -\frac{1}{6})\) pattern. Upon annealing to 1050 K, however, the background signal decreases.

Fig. 7. LEED patterns observed following adsorption of silane at 350 K and annealing to 1050 K. Representative substrate diffraction features are indicated by arrows. Schematics of the LEED patterns and the real space unit cells are also shown. In the schematic drawings, substrate features are shown by open circles while overlayer features are shown by closed circles. In the real space drawings, only tungsten atoms are shown. LEED patterns, beam energies and silicon coverages are (a) complex, 210 eV and 0.44 ML; (b) \((-\frac{4}{5}, -\frac{4}{5})\), 224 eV and 0.83 ML; (c) \((-\frac{5}{6}, -\frac{1}{6})\), 231 eV and 1.0 ML. Fig. 7d shows the LEED pattern observed after annealing a monolayer of silane to 1050 K, adsorbing an additional 6 L of silane at 350 K, and annealing to 1050 K (beam energy = 142 eV).
dramatically, and very sharp streaks appear between the substrate spots in the [110] direction (fig. 7d). These streaks remain even after many cycles of adsorption at 350 K followed by annealing to 1050 K.

Silane adsorption at 120 K produces no new features in the LEED pattern. The only effect of silane adsorption at 120 K is to increase the background signal of the LEED pattern. Annealing to 1050 K following silane adsorption at 120
K results in the same LEED patterns which are observed for comparable Si/W ratios following adsorption at 350 K and annealing to 1050 K.

4. Discussion

4.1. Adsorption at 350 K

4.1.1. Hydrogen TPD

From the variations in the silicon coverage and hydrogen TPD as a function of silane exposure, it can be seen that the ratio of hydrogen to silicon on the surface decreases from 3:1 to 1:10 as the silicon coverage increases from 0.27 to 1.0. Thus, following a saturation dose, less than three percent of the hydrogen which arrived at the surface as silane remains. The absence of a significant amount of hydrogen on the surface following a saturation exposure clearly indicates that silane undergoes complete dissociation on W(110) at 350 K. The 0.10 ML of hydrogen which remain at saturation may be located at defect sites, or alternatively, some hydrogen spillover from the tungsten surface to sites on top of the silicon adlayer may be occurring.

The displacement of hydrogen by silicon indicates that silicon and hydrogen atoms adsorb competitively on W(110). Hydrogen and silicon atoms must therefore preferentially adsorb either at the same surface site, or in differing sites which are close enough together to result in steric interactions between the two adsorbates. For small silane exposures, enough atomic adsorption sites are available for both the silicon atoms and the hydrogen atoms generated by dissociation, and so little displacement of hydrogen occurs. For higher exposures, however, the total number of hydrogen and silicon atoms generated by dissociation exceeds the number of adsorption sites, and hydrogen atoms, being the more weakly bound species, are displaced from the surface.

Thermal desorption of hydrogen following exposure of the W(110) surface to silane at 350 K shows only a single peak at 400 K. Since silane dissociates completely at 350 K, this peak is almost certainly due to associative desorption of adsorbed hydrogen atoms. Comparison with the associative desorption of hydrogen from clean W(110) shows that the presence of silicon lowers the hydrogen desorption temperature by 50–100 K. This change in desorption temperature suggests an interaction between silicon and hydrogen atoms which decreases the adsorption energy of hydrogen. Changes in the preexponential factor for desorption could also be responsible for the decrease in desorption temperature.

4.1.2. LEED

For silicon coverages below 0.20 ML, only a (1X1) pattern is observed following adsorption at 350 K, indicating either random adsorption of silicon atoms at these coverages, or the presence of ordered domains or islands which are too small to be seen with LEED. For a silicon coverage of 0.27 ML a (1\_1) pattern with the overlayer spots broadened in the [\_10] direction is observed after silane adsorption at 350 K. The fact that broadening occurs only in the [\_10] direction indicates a strong interaction between silicon atoms in the [001] direction, with very weak interactions in the [\_10] direction. The structure giving rise to the (1\_1) pattern is therefore proposed to consist of rows of silicon atoms in the [001] direction, separated by the lattice spacing of the W(110) substrate. The spacing between these rows is essentially random, with a slight preference for a spacing equal to the substrate spacing in the [\_10] direction. Random spacing of the silicon rows would result in regions of the surface which are essentially free of silicon. Evidence for such regions is shown in fig. 2a, which exhibits a high temperature shoulder corresponding roughly to hydrogen desorption from clean W(110). The presence of this shoulder suggests that silicon-free regions of W(110) are present following small silane exposures, and that hydrogen atoms formed by silane dissociation can migrate to these regions.

Upon annealing 0.27 ML of silicon to 700 K, all of the hydrogen desorbs and a (1\_2) LEED pattern is formed. This pattern has the unit cell shown in fig. 6a. By placing one atom at each corner of the unit cell a coverage of 0.25 ML is obtained, in excellent agreement with the experimentally determined coverage of 0.27 ML. Thus,
the entire surface is covered by the \((1_{-1}^{\frac{1}{2}})\) structure. Formation of the \((1_{-1}^{\frac{1}{2}})\) structure from the disordered \((1_{-1}^{\frac{1}{2}})\) structure involves movement of adsorbed silicon atoms over many lattice spacings. At 700 K silicon atoms should have the required mobility to affect this transformation since FIM studies [10] have shown that silicon atoms become mobile on W(110) above 250 K.

A \((1_{-1}^{\frac{1}{2}})\) structure has been seen previously by Casanova and Tsong for silicon adsorbed on W(110) using field ion microscopy [10]. Fink and Ehrlich [8] also observed an ordered structure for silicon on W(110) using FIM which they identify as a \((1_{-1}^{\frac{1}{2}})\) pattern. This pattern is similar to the \((1_{-1}^{\frac{1}{2}})\) pattern reported here, except that there are three spacings between rows in the [001] direction, rather than two. Upon careful examination of the ion image presented in fig. 4 of Fink and Ehrlich’s paper [8], however, it is not clear that the resolution is sufficient to distinguish between the \((1_{-1}^{\frac{1}{2}})\) and \((1_{-1}^{\frac{1}{2}})\) structures. Thus, the results presented here are consistent with both FIM studies [8,10].

The \((1_{-1}^{\frac{1}{2}})\) structure observed immediately after adsorption at 350 K was not observed in the FIM studies [8,10]. In the FIM studies, however, silicon was deposited by resistive heating of a silicon wafer [10] so that no hydrogen was present following adsorption. In the absence of hydrogen, the driving force for formation of silicon chains was absent and only the \((1_{-1}^{\frac{1}{2}})\) structure was observed.

As discussed in section 3.3, the rearrangement of silicon atoms upon annealing to 700 K can be attributed to removal of hydrogen from the surface. The tendency for silicon atoms to disperse from closely packed rows of silicon atoms into the more uniform \((1_{-1}^{\frac{1}{2}})\) structure upon removal of hydrogen suggests a repulsive interaction between adsorbed silicon atoms. The source of this repulsion is unclear. Partial charge transfer from tungsten to silicon, resulting in an electrostatic repulsion, is unlikely given the very small electronegativity difference between tungsten and silicon [28]. A strong steric effect is also unlikely given that the covalent radius of silicon is less than that of tungsten. The repulsion therefore appears to be due to a through-surface interaction which results in adsorption at nearest neighbor sites being less favorable than at next nearest neighbor sites.

Prior to annealing to 700 K, an additional force must exist which can overcome the repulsion between silicon atoms and result in the formation of chains of silicon atoms in the [110] direction. This force could be due to attractive Si–H–Si interactions, i.e., hydrogen atoms bridge bonding to two silicon atoms. Because the distance between adjacent silicon adsorption sites in the [110] direction is larger than in the [001] direction, such a bridging interaction would be expected to be weaker in the [110] direction. Thus, for low silicon coverages, an attractive bridging interaction would result in the observed formation of long chains of silicon atoms in the [001] direction, with little order in the [110] direction.

For 0.44 ML of silicon, a well ordered \((1_{-1}^{\frac{1}{2}})\) pattern is observed following adsorption at 350 K. For a coverage of 0.59 ML, the \((1_{-1}^{\frac{1}{2}})\) pattern is replaced by a \((1_{-1}^{\frac{1}{2}})\) pattern, indicating that the maximum coverage for the \((1_{-1}^{\frac{1}{2}})\) pattern is roughly 0.5 ML. By placing one silicon atom in each corner of the \((1_{-1}^{\frac{1}{2}})\) unit cell, this maximum coverage can be achieved. Thus, the \((1_{-1}^{\frac{1}{2}})\) structure is proposed to consist of rows of silicon atoms in the [001] direction with every other row of long bridge sites unoccupied (fig. 5a). Although the silicon atoms have been positioned in the long bridge sites in fig. 5a, they could equally well be located in the pseudo-threefold hollow sites. Adsorption in any other site is unlikely since atomic adsorbates generally adsorb in sites of highest coordination [40]. The higher degree of ordering in the [110] direction for 0.44 ML as opposed to 0.27 ML is simply due to the increased coverage. In order to accommodate 0.44 ML of silicon, very few empty rows can exist between the filled rows of silicon atoms.

Annealing 0.44 ML of silicon to 700 K removes hydrogen from the surface, and results in a \((2_{-1}^{\frac{1}{2}})\) LEED pattern which has the real space unit cell shown in fig. 6b. By placing only one silicon atom in this unit cell, the maximum coverage which can be obtained is 0.25 ML, well below the actual coverage of 0.44 ML. Thus, it is necessary to place two silicon atoms in each unit cell, resulting in a local coverage of 0.5 ML. The overall silicon coverage is only slightly less than 0.5 ML, so that nearly the entire surface is covered by the \((2_{-1}^{\frac{1}{2}})\)
structure. One possible \( (2^2_1) \) structure, shown in fig. 6b, has silicon atoms at each corner of the unit cell, with two additional silicon atoms located in pseudo-threefold hollow sites on the long edges of the unit cell. This structure is very similar to the \( (1^1_1) \) structure, except that the rows of silicon atoms have paired up. While other \( (1^1_1) \) structures are possible, all reasonable alternatives involve some type of clustering or pairing of silicon atoms.

The transformation from the \( (1^1_1) \) pattern formed at 350 K to the \( (2^2_1) \) pattern is again attributed to interactions between hydrogen and silicon atoms. Because nearly the entire surface is covered by the \( (1^1_1) \) structure when 0.44 ML of silicon are present, the removal of hydrogen by annealing to 700 K cannot result in dispersal of the silicon chains as is the case for 0.27 ML. The presence of hydrogen does, however, cause the silicon atoms to adopt the symmetric \( (2^2_1) \) structure rather than the \( (2^2_1) \) structure. The mechanism by which hydrogen induces this change in structure is unclear. The pairing or clustering of silicon atoms in the absence of hydrogen seems to be inconsistent with the repulsive interactions between silicon atoms postulated earlier. Evidently, when high coverages force the silicon atoms into close proximity, the nature of the Si-Si interactions are such that pairing or clustering is more favorable than a more symmetric distribution. The \( (2^2_1) \) pattern was not reported in either of the FIM studies [8, 10], possibly because the silicon coverages employed in those studies were not high enough.

After adsorbing silane at 350 K to deposit 0.59 ML of silicon, the \( (1^1_1) \) spots remain, but new spots indicative of a \( (2^2_1) \) pattern can also be seen. (Note that this \( (2^2_1) \) structure is distinct from the \( (2^2_1) \) structure observed for 0.27 ML of silicon annealed to 700 K.) The \( (2^2_1) \) spots grow in intensity and sharpness when the coverage is increased to 0.72 ML. Since the unit cell for the \( (2^2_1) \) structure contains four substrate atoms (fig. 5b), at least three silicon atoms must be present in order to achieve the required coverages. Many \( (2^2_1) \) structures are possible which are consistent with the data, and one possible structure is shown in fig. 6c. Transformation of the \( (2^2_1) \) structure of fig. 5b into the \( (2^2_1) \) structure suggested in fig. 6c involves displacement of adsorbed silicon atoms over several lattice spacings. As pointed out above, 700 K is a high enough temperature for the silicon atoms to have the required mobility [10].

Following a saturation silane exposure at 350 K, a p(2 \( \times \) 2) pattern is observed with broadening or splitting of the half order spots in directions perpendicular to the reciprocal lattice vectors of the substrate. In addition, small rings can be seen around the substrate spots. The presence of the rings and the broadening indicate some type of disorder in the overlayer. The direction of the broadening, however, is perpendicular to the direction normally observed for a disordered overlayer. Normally, the elongation of half order spots due to disorder is parallel to the reciprocal lattice vectors of the substrate [41]. The cause of this unusual broadening is not understood at present.

The only known p(2 \( \times \) 2) structure for a monolayer of silicon on W(110) is shown in fig. 5c. This structure, first proposed for the second layer of chromium atoms on W(110) [42], consists of groups of four silicon atoms clustered about a tungsten atom. As for the \( (2^2_1) \) structure, the nature of the Si-Si interactions are apparently such that at high coverages, clustering is favored over a more symmetric distribution. The transition from the \( (2^2_1) \) pattern observed for slightly lower coverages into the p(2 \( \times \) 2) structure involves only small movements of silicon atoms from bridge sites to pseudo-threefold hollow sites, and adsorption of additional silicon atoms at unoccupied threefold hollow sites.
Upon annealing a monolayer of silicon to 700 K, the \( p(2 \times 2) \) pattern remains visible, but broadening of the overlayer spots in the [110] direction is apparent, again indicating the presence of disorder in this direction. As discussed in section 3.1, some diffusion of silicon into the tungsten substrate occurs upon annealing to 700 K. Thus, the coverage of silicon on the surface is less than a full monolayer following the anneal, and disorder in the [110] direction results.

Upon annealing silicon overlayers to 1050 K dramatic changes occur in the LEED patterns for all coverages. In all cases, the changes can be attributed to silicide formation, as discussed in section 3.4. For coverages \( \geq 0.59 \) ML, the unit cells of the overlayer structures are much larger than the substrate unit cell, suggesting that the LEED patterns are due to the formation of coincidence lattices, i.e., the silicide layers grow epitaxially on the W(110) substrate such that the dimensions of the substrate and overlayer unit cells are related by a ratio of integers \([41]\). Consequently, when attempting to assign structures to the silicide overlayers it will be helpful to compare the dimensions of the overlayer unit cells to the unit cell dimensions of various crystal planes of tungsten silicides.

Upon annealing up to 0.44 ML of silicon to 1050 K, the complex LEED pattern of fig. 7a is observed. Careful examination of fig. 7a indicates that no primitive unit cell can be drawn for the overlayer reciprocal lattice. Thus, it is likely that this LEED pattern is the superposition of at least two different LEED patterns, corresponding to either rotational degeneracy or two different overlayer structures. Because of the extreme complexity of fig. 7a no attempt will be made to propose a structure for this pattern.

For all coverages between 0.59 ML and 0.83 ML, annealing to 1050 K produces a \( c_{1-\frac{a}{2}} \) pattern. The real space unit cell of this pattern is rectangular with dimensions of 15.8 Å in the [001] direction and 17.9 Å in the [110] direction. Comparison with the unit cell dimensions of WSi\(_2\) [43], W\(_8\)Si\(_3\) [44] and W\(_6\)Si [45] shows that the unit cell of the \( c_{1-\frac{a}{2}} \) pattern cannot be filled with the low index planes of any of these silicides without significant lattice strain. Thus, the \( c_{1-\frac{a}{2}} \) structure may be due to a high index plane of one of the tungsten silicides, or to a surface silicide structure which is not stable as a bulk compound.

Annealing a monolayer of silicon to 1050 K forms a \( (0\overline{1}0) \) pattern, which has the unit cell shown in fig. 7c. The overlayer unit cell, shown in fig. 7c, is approximately square, with sides 15.6 Å long. A comparison with the body centered tetragonal structure of WSi\(_2\) [43] shows that 15.6 Å is approximately twice as long as the \( c \) dimension and five times as long as the \( a \) dimension of WSi\(_2\) (fig. 8). Thus, two possible structures for the WSi\(_2\) overlayer can be proposed. In one, the unit cell is filled by (001) planes of WSi\(_2\). These planes consist of a square array of tungsten atoms, spaced 3.12 Å apart, with silicon atoms centered in the tungsten squares, approximately 1.3 Å below (or above) the plane of the tungsten atoms. In the other structure, the unit cell is filled by (100) planes of WSi\(_2\), which consist of a 3.12 Å \( \times \) 7.80 Å rectangular array of tungsten atoms with two silicon atoms located between the tungsten atoms on the long edges of the rectangles. Note that in both cases the WSi\(_2\) overlayer is strained slightly due to small mismatches in the lattice parameters and the fact that the overlayer lattice is not exactly square. Without measurement and analysis...
of \(I-V\) curves, no choice can be made between the two possibilities.

Adsorption of silane on top of the \((-1, -1)\) structure at 350 K, followed by annealing to 1050 K results in the addition of streaks between the substrate spots in the [\(\bar{1}10\)] direction (fig. 7d). After several cycles of adsorption at 350 K followed by annealing to 1050 K, the Si/W AES ratio becomes constant, indicating the formation of a stoichiometric compound of silicon and tungsten. This stoichiometric compound is most likely WSi\(_2\) since it was shown above that a \((-1, -1)\) structure can be formed by low index planes of WSi\(_2\) growing epitaxially on W(110). The streaking observed in fig. 7d cannot be due to disorder in the \((-1, -1)\) structure since not all of the overlayer features are streaked. The pattern in fig. 7d must therefore be a superposition of the \((-1, -1)\) pattern with a second pattern having a periodicity of one lattice spacing in the [001] direction and little or no order in the [\(\bar{1}10\)] direction. This second pattern may be the result of relaxation of the silicide multilayers in order to relieve the small strain which is present in the first layer. This relaxation could conceivably result in a buckling or reconstruction at the surface of the silicide giving rise to the streaks.

4.2. Adsorption at 120 K

Comparison of the Si(92 eV) lineshapes and the hydrogen TPD spectra following adsorption of silane on W(110) at 350 K versus 120 K clearly indicates that different processes are occurring in the two cases. In section 3.2 it was suggested that while complete dissociation occurs at 350 K, only partial dissociation occurs at 120 K resulting in a stable SiH\(_x\) species. It was also shown that both the TPD and Auger data are consistent with the presence of 0.25–0.30 ML of silicon on the surface. Finally, LEED demonstrates that no ordering of the overlayer occurs at 120 K. Based on these observations, the stoichiometry of the species formed at 120 K can be tentatively determined.

In order to satisfy the valence of silicon, it will be assumed that an SiH\(_x\) species can bind to only one surface tungsten atom, and must therefore be located at an atop site. Similarly, an SiH\(_2\) species can bind to two surface atoms and must be located at a bridge site. Using known values of the Si–H bond length [46] and the covalent radius of hydrogen atoms [28], the projection of an SiH\(_2\) group onto a flat surface can be calculated. The projection is approximately circular with a diameter of 3.38 Å. In comparison, the W–W nearest neighbor distance on W(110) is 2.74 Å, while the next nearest neighbor distance is 3.16 Å. Because the diameter of the projection of SiH\(_3\) is greater than both the nearest neighbor and next-nearest neighbor distances on W(110), adsorption of SiH\(_3\) at an atop site would prevent adsorption of a second SiH\(_3\) at both the four nearest neighbor sites and the two next-nearest neighbor sites. Using this information, a Monte Carlo simulation was performed with a 400 atom bcc(110) array, allowing SiH\(_3\) species to adsorb randomly at unblocked atop sites until all available adsorption sites were either filled or blocked by neighboring SiH\(_x\) groups. The maximum coverage predicted by the simulation is 0.25 ML, in excellent agreement with the experimentally determined coverage of 0.25–0.30 ML. Note that random adsorption of 0.25 ML of SiH\(_3\) leaves an adequate number of sterically uninhibited adsorption sites for the hydrogen atoms produced by dissociation. The projections of both SiH\(_2\) and SiH species onto the surface would obviously be smaller than that of SiH\(_3\), so that steric considerations alone would predict higher coverages if either of these species were formed at 120 K. Thus, the partially dissociated species formed at 120 K can be tentatively identified as SiH\(_3\). Formation of SiH\(_3\) by dissociation of silane has been reported on the Si(111)-(7 \(\times\) 7) surface [31]. Additional work is clearly required in order to confirm this assignment.

Thermal desorption of H\(_2\) following silane adsorption at 120 K exhibits three features at 250, 300 and 400 K (fig. 4). The feature at 400 K is also observed following adsorption of silane at 350 K, and was earlier attributed to recombinative desorption of H\(_{\text{ad}}\) from silicon covered W(110). The lower temperature peaks, which are not observed following adsorption at 350 K, are believed to indicate the onset of SiH\(_x\) decomposition. As noted above, 0.25–0.30 ML of SiH\(_x\) are formed upon adsorption at 120 K. Complete decomposition of
0.25 ML of silane would result in 1.0 ML of $H_{(a)}$ as well as 0.25 ML of silicon. Since silicon and hydrogen atoms adsorb competitively, not enough sites are available to accommodate all of the silicon and hydrogen atoms, and at least 0.25 ML of $H_{(a)}$ must recombine and desorb upon SiH$_x$ decomposition. Although overlap of the desorption features in fig. 4b makes a determination of the relative sizes of the three peaks difficult, visual inspection of fig. 4b shows that the two low temperature peaks could quite reasonably contain 25% of the total hydrogen desorption. Thus, TPD is consistent with decomposition of the SiH$_x$ species in the range 200–300 K. Hydrogen atoms which do not desorb upon SiH$_x$ decomposition remain on the surface until undergoing recombintive desorption at 400 K. The decomposition temperature of SiH$_x$ on W(110) is well below the corresponding temperature of 473 K on Ni(111) [16]. Since tungsten is generally a more reactive metal than nickel, it is not surprising that complete dissociation of silane would occur at a lower temperatures on tungsten than on nickel.

5. Conclusion

Silane undergoes complete dissociation on W(110) at 350 K. Dissociation continues at 350 K until a monolayer of silicon has been deposited, at which point the dissociative sticking probability decreases by at least two orders of magnitude. The hydrogen atoms formed by the dissociation are displaced by silicon atoms at high exposures. Dissociation appears to occur via a mobile precursor. At 120 K, only partial dissociation occurs to form a surface species tentatively identified as SiH$_3$. Up to 0.25 ML of SiH$_3$ can be formed before steric interactions prevent further SiH$_3$ formation. The SiH$_3$ species decomposes to silicon and hydrogen atoms between 200 and 300 K. A wide variety of LEED patterns are formed by silicon overlayers, depending on both the silicon coverage and the presence of hydrogen on the surface.

Upon heating to 1050 K, silicon diffuses into the tungsten substrate, forming tungsten silicides. The formation of these silicides results in complex LEED patterns which indicate that the silicides grow epitaxially on W(110) in coincidence lattices. By sequentially exposing the surface to silane at 350 K and annealing to 1050 K, thick, stoichiometric WSi$_x$ layers can be epitaxially grown on W(110).

The ability to grow stoichiometric tungsten silicide films by reaction of tungsten with silane has potential applications for CVD of tungsten silicide [1]. Silicon modified tungsten surfaces also have interesting properties with regard to corrosion inhibition [19] and heterogeneous catalysis [21,22]. The catalytic aspects of silicon modified tungsten surfaces will be examined in a subsequent paper [23].

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References

The covalent radius of silicon will be used throughout this paper. The nearly equal electronegativities of silicon and tungsten \[28\] suggest that the tungsten-silicon bond will be primarily covalent rather than ionic.


